

We claim:-

1. An aqueous dispersion of a copolymer obtainable by free radical copolymerization of

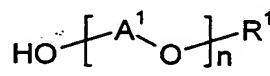
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- (A) at least one ethylenically unsaturated dicarboxylic anhydride, derived from at least one dicarboxylic acid of 4 to 8 carbon atoms,
- (B) at least one oligomer of branched or straight-chain C<sub>3</sub>-C<sub>10</sub>-alkene, at least one oligomer having an average molecular weight M<sub>n</sub> of from 300 to 10 5 000 g/mol or being obtainable by oligomerization of at least 3 equivalents of C<sub>3</sub>-C<sub>10</sub>-alkene,
- (C) optionally at least one ethylenically unsaturated comonomer differing from (A),

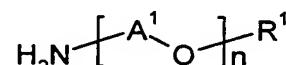
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15 and optionally reaction with

- (D) at least one compound of the formula I a or I b



I a



I b

20

and subsequent addition of water,

where, in formulae I a and I b,

A<sup>1</sup> are identical or different C<sub>2</sub>-C<sub>20</sub>-alkylene,

R<sup>1</sup> are linear or branched C<sub>1</sub>-C<sub>30</sub>-alkyl, phenyl or hydrogen, and

25

n is an integer from 1 to 200,

the water content being from 30 to 99.5% by weight, based on aqueous dispersion.

30 2. The aqueous dispersion according to claim 1, wherein some or all of the anhydride group of the copolymer are hydrolyzed with water or an aqueous alkaline solution after the polymerization.

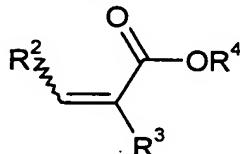
35 3. The aqueous dispersion according to either of claims 1 and 2, wherein the molar ratios of comonomers incorporated in the form of polymerized units in the copolymer are as follows:

- (A) from 5 to 60 mol%,

(B) from 1 to 95 mol%,  
 (C) from 0 to 70 mol%, based in each case on copolymer, the sum of (A), (B) and (C) being 100 mol%, and  
 (D) from 0 to 50 mol%, based on all carboxyl groups of the copolymer.

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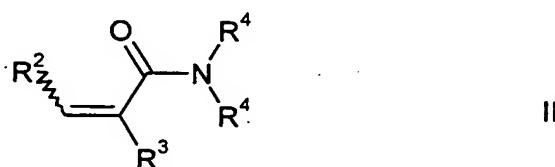
4. The aqueous dispersion according to any of claims 1 to 3, wherein (C) is selected from ethylenically unsaturated C<sub>3</sub>-C<sub>8</sub>-carboxylic acid derivatives of the formula II



II

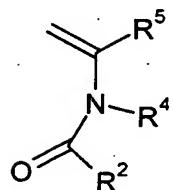
carboxamides of the formula III

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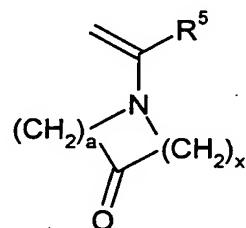


III

acyclic amides of the formula IV a or cyclic amides of the formula IV b



IV a



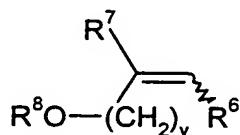
IV b

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C<sub>1</sub>-C<sub>20</sub>-alkyl vinyl ethers,  
 N-vinyl derivatives of nitrogen-containing aromatic compounds,  
 α,β-unsaturated nitriles,

20

alkoxylated unsaturated ethers of the formula V

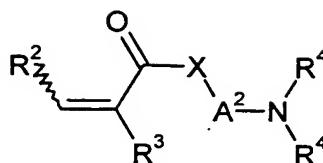


V

25

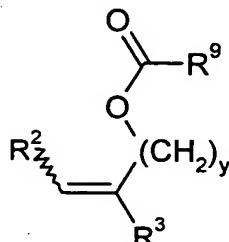
esters or amides of the formula VI

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VI

unsaturated esters of the formula VII



VII

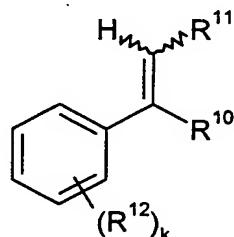
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comonomers containing phosphate; phosphonate, sulfate and sulfonate groups,

alpha-olefins of 3 to 40 carbon atoms,

10

vinylaromatic compounds of the formula VIII



VIII

15

where, in the formulae,

A<sup>2</sup> and A<sup>3</sup> are identical or different and are C<sub>2</sub>-C<sub>20</sub>-alkylene,R<sup>2</sup> and R<sup>3</sup> are identical or different and are selected from hydrogen, straight-chain or branched C<sub>1</sub>-C<sub>5</sub>-alkyl and COOR<sup>4</sup>,20 R<sup>4</sup> are identical or different and are selected from hydrogen and branched or straight-chain C<sub>1</sub>-C<sub>22</sub>-alkyl,R<sup>5</sup> is hydrogen or methyl,

x is an integer from 2 to 6,

y is an integer selected from 0 and 1,

25 a is an integer from 0 to 6,

b is an integer from 1 to 200,

R<sup>6</sup> and R<sup>7</sup> are identical or different and are selected from hydrogen and straight-chain or branched C<sub>1</sub>-C<sub>10</sub>-alkyl,  
X is oxygen or N-R<sup>4</sup>  
R<sup>8</sup> is [A<sup>3</sup>-O]<sub>b</sub>-R<sup>4</sup>,  
5 R<sup>9</sup> are identical or different and are selected from hydrogen and straight-chain or branched C<sub>1</sub>-C<sub>10</sub>-alkyl,  
R<sup>10</sup> and R<sup>11</sup>, independently of one another, are hydrogen, methyl or ethyl,  
R<sup>12</sup> is selected from methyl and ethyl,  
k is an integer from 0 to 2  
10 and the remaining variables are defined as above.

5. The aqueous dispersion according to any of claims 1 to 4, which comprises at least one oligomer of branched or straight-chain C<sub>3</sub>-C<sub>10</sub>-alkene, at least one oligomer having an average molecular weight M<sub>n</sub> of from 300 to 5 000 g/mol or being obtainable by oligomerization of at least 3 equivalents of C<sub>3</sub>-C<sub>10</sub>-alkene.  
15  
6. A process for the preparation of an aqueous dispersion according to any of claims 1 to 5, wherein (A) and (B) and, if appropriate, (C) are subjected to free radical copolymerization with one another and then water is added.  
20  
7. The process according to claim 6, wherein reaction with (D) is effected during or after the copolymerization of (A), (B) and, if required, (C).  
25  
8. The use of an aqueous dispersion according to any of claims 1 to 5 for the treatment of fibrous substrates.  
  
9. A process for the treatment of fibrous substrates using an aqueous dispersion according to any of claims 1 to 5.  
30  
10. The process according to claim 9, wherein fibrous substrates are selected from leather, textile, paper, board, wood, wood composites, artificial leather, alcantara and lefa.  
  
35  
11. The process according to claim 10, wherein the leather is wet-white.  
  
12. A fibrous substrate treated by a process according to any of claims 9 to 11.  
  
13. The fibrous substrate according to claim 12, wherein said substrate is leather.  
40

14. The leather according to claim 13, wherein said leather is based on wet-white.

15. The use of a fibrous substrate according to any of claims 12 to 14 for the production of articles of clothing or pieces of furniture or automotive parts.

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16. A copolymer obtainable by free radical copolymerization of

(A) at least one ethylenically unsaturated dicarboxylic anhydride, derived from at least one dicarboxylic acid of 4 to 8 carbon atoms,

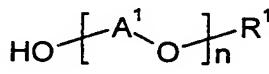
10 (B) at least one oligomer of branched or straight-chain C<sub>3</sub>-C<sub>10</sub>-alkene, at least one oligomer having an average molecular weight M<sub>n</sub> of from 300 to 5 000 g/mol or being obtainable by oligomerization of at least 3 equivalents of C<sub>3</sub>-C<sub>10</sub>-alkene,

15 (C) optionally at least one ethylenically unsaturated comonomer differing from (A),

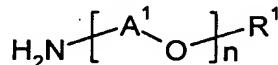
and reaction with

(D) at least one compound of the formula I a or I b

20



I a



I b

where, in formulae I a and I b,

25 A<sup>1</sup> are identical or different C<sub>2</sub>-C<sub>20</sub>-alkylene,

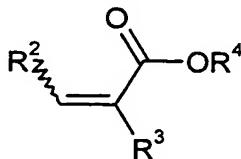
R<sup>1</sup> is linear or branched C<sub>1</sub>-C<sub>30</sub>-alkyl, phenyl or hydrogen, and

n is an integer from 1 to 200,

and optionally hydrolysis.

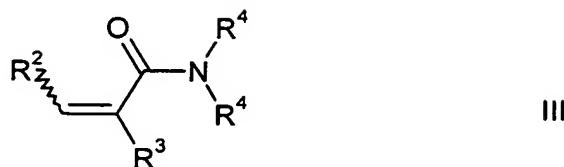
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17. The copolymer according to claim 16, wherein (C) is selected from ethylenically unsaturated C<sub>3</sub>-C<sub>8</sub>-carboxylic acid derivatives of the formula II

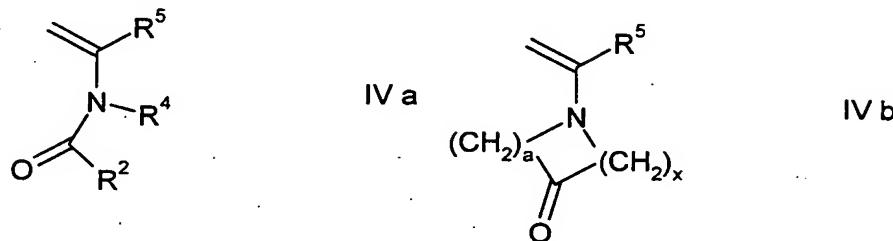


II

carboxamides of the formula III



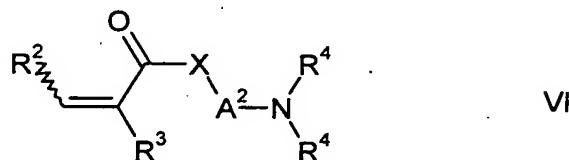
5 acyclic amides of the formula IV a or cyclic amides of the formula IV b



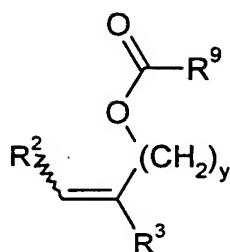
10  $C_1-C_{20}$ -alkyl vinyl ethers,  
 N-vinyl derivatives of nitrogen-containing aromatic compounds,  
 $\alpha,\beta$ -unsaturated nitriles,  
 alkoxyated unsaturated ethers of the formula V



15 esters or amides of the formula VI



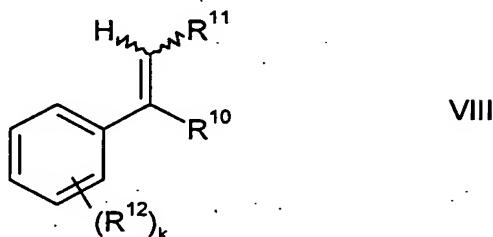
20 unsaturated esters of the formula VII



comonomers containing phosphate, phosphonate, sulfate and sulfonate groups,

5        $\alpha$ -olefins of 3 to 40 carbon atoms,

vinylic aromatic compounds of the formula VIII



10       where, in the formulae,

A<sup>2</sup> and A<sup>3</sup>   are identical or different and are C<sub>2</sub>-C<sub>20</sub>-alkylene,

15       R<sup>2</sup> and R<sup>3</sup>   are identical or different and are selected from hydrogen, straight-chain or branched C<sub>1</sub>-C<sub>5</sub>-alkyl and COOR<sup>4</sup>,

R<sup>4</sup>       are identical or different and are selected from hydrogen and branched or straight-chain C<sub>1</sub>-C<sub>22</sub>-alkyl,

R<sup>5</sup>       is hydrogen or methyl,

x           is an integer from 2 to 6,

20       y           is an integer selected from 0 and 1,

a           is an integer from 0 to 6,

b           is an integer from 1 to 200,

25       R<sup>6</sup> and R<sup>7</sup>   are identical or different and are selected from hydrogen and straight-chain or branched C<sub>1</sub>-C<sub>10</sub>-alkyl,

X           is oxygen or N-R<sup>4</sup>

R<sup>8</sup>       is [A<sup>3</sup>-O]<sub>b</sub>-R<sup>4</sup>,

R<sup>9</sup>       are identical or different and are selected from hydrogen and straight-chain or branched C<sub>1</sub>-C<sub>10</sub>-alkyl,

R<sup>10</sup> and R<sup>11</sup>, independently of one another, are hydrogen, methyl or ethyl,

30       R<sup>12</sup>       is selected from methyl and ethyl,

k is an integer from 0 to 2

and the remaining variables are defined as above.

- 5    18. The use of a copolymer according to claim 16 or 17 for the treatment of fibrous substrates.
- 10    19. The use of an aqueous dispersion according to any of claims 1 to 5 or a copolymer according to claim 16 or 17 for the impregnation of sheet-like substrates.
- 15    20. A process for the impregnation of sheet-like substrates, wherein a sheet-like substrate is treated with an aqueous dispersion according to any of claims 1 to 5 or with a copolymer according to claim 16 or 17.
21. The process according to claim 20, wherein the sheet-like substrate is concrete or brick.

Aqueous dispersions of copolymers, production thereof and use of the same

**Abstract**

5 Aqueous dispersions of copolymers are obtainable by free radical copolymerization of  
 (A) at least one ethylenically unsaturated dicarboxylic anhydride, derived from at  
 least one dicarboxylic acid of 4 to 8 carbon atoms,  
 (B) at least one oligomer of branched or straight-chain C<sub>3</sub>-C<sub>10</sub>-alkene, at least one  
 10 oligomer having an average molecular weight M<sub>n</sub> of from 300 to 5 000 g/mol or  
 being obtainable by oligomerization of at least 3 equivalents of C<sub>3</sub>-C<sub>10</sub>-alkene,  
 (C) optionally at least one ethylenically unsaturated comonomer differing from (A),

and optionally reaction with

15 (D) at least one compound of the formula I a or I b



I a

I b

and subsequent addition of water,

20 where, in formulae I a and I b,  
 A<sup>1</sup> are identical or different C<sub>2</sub>-C<sub>20</sub>-alkylene,  
 R<sup>1</sup> is linear or branched C<sub>1</sub>-C<sub>30</sub>-alkyl, phenyl or hydrogen, and  
 n is an integer from 1 to 200,  
 25 the water content being from 30 to 99.5% by weight, based on aqueous dispersion.

## New claims

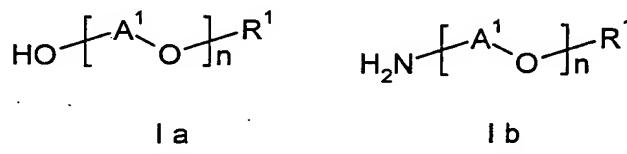
1. An aqueous dispersion of a copolymer obtainable by free radical copolymerization of

5

- (A) at least one ethylenically unsaturated dicarboxylic anhydride, derived from at least one dicarboxylic acid of 4 to 8 carbon atoms,
- (B) at least one oligomer of isobutene, at least one oligomer having an average molecular weight  $M_n$  of from 300 to 5 000 g/mol,
- 10 (C) optionally at least one ethylenically unsaturated comonomer differing from (A),

and reaction with

15 (D) at least one compound of the formula I a or I b



and subsequent addition of water,

20 where, in formulae I a and I b,

$\text{A}^1$  are identical or different  $\text{C}_2\text{-C}_{20}$ -alkylene,

$\text{R}^1$  are linear or branched  $\text{C}_1\text{-C}_{30}$ -alkyl, phenyl or hydrogen, and

$n$  is an integer from 1 to 200,

25 the water content being from 30 to 99.5% by weight, based on aqueous dispersion.

2. The aqueous dispersion according to claim 1, wherein some or all of the anhydride group of the copolymer are hydrolyzed with water or an aqueous 30 alkaline solution after the polymerization.

3. The aqueous dispersion according to either of claims 1 and 2, wherein the molar ratios of comonomers incorporated in the form of polymerized units in the copolymer are as follows:

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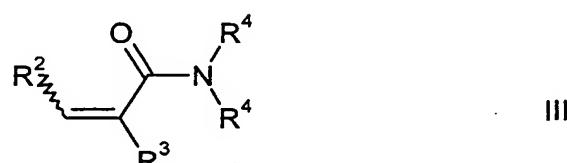
- (A) from 5 to 60 mol%,
- (B) from 1 to 95 mol%,

(C) from 0 to 70 mol%, based in each case on copolymer, the sum of (A), (B) and (C) being 100 mol%, and  
 (D) from 0 to 50 mol%, based on all carboxyl groups of the copolymer.

5 4. The aqueous dispersion according to any of claims 1 to 3, wherein (C) is selected from ethylenically unsaturated C<sub>3</sub>-C<sub>8</sub>-carboxylic acid derivatives of the formula II

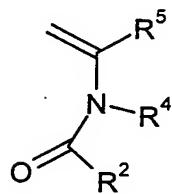


carboxamides of the formula III

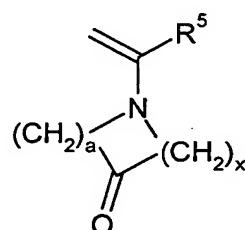


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acyclic amides of the formula IV a or cyclic amides of the formula IV b



IV a



IV b

15

C<sub>1</sub>-C<sub>20</sub>-alkyl vinyl ethers,  
 N-vinyl derivatives of nitrogen-containing aromatic compounds,  
 α,β-unsaturated nitriles,

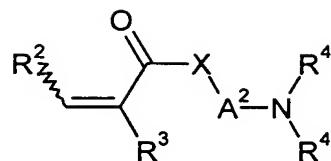
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alkoxylated unsaturated ethers of the formula V

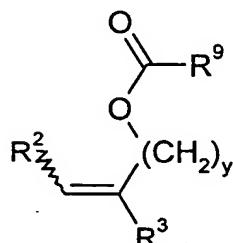


esters or amides of the formula VI

25



unsaturated esters of the formula VII



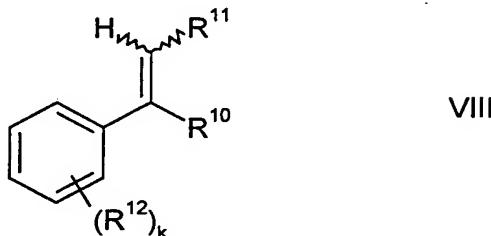
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comonomers containing phosphate, phosphonate, sulfate and sulfonate groups,

$\alpha$ -olefins of 3 to 40 carbon atoms,

10

vinylic aromatic compounds of the formula VIII



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where, in the formulae,

A<sup>2</sup> and A<sup>3</sup> are identical or different and are C<sub>2</sub>-C<sub>20</sub>-alkylene,

R<sup>2</sup> and R<sup>3</sup> are identical or different and are selected from hydrogen, straight-chain or branched C<sub>1</sub>-C<sub>5</sub>-alkyl and COOR<sup>4</sup>,

20 R<sup>4</sup> are identical or different and are selected from hydrogen and branched or straight-chain C<sub>1</sub>-C<sub>22</sub>-alkyl,

R<sup>5</sup> is hydrogen or methyl,

x is an integer from 2 to 6,

y is an integer selected from 0 and 1,

25 a is an integer from 0 to 6,

b is an integer from 1 to 200,

R<sup>6</sup> and R<sup>7</sup> are identical or different and are selected from hydrogen and straight-chain or branched C<sub>1</sub>-C<sub>10</sub>-alkyl,  
X is oxygen or N-R<sup>4</sup>  
R<sup>8</sup> is [A<sup>3</sup>-O]<sub>b</sub>-R<sup>4</sup>,  
5 R<sup>9</sup> are identical or different and are selected from hydrogen and straight-chain or branched C<sub>1</sub>-C<sub>10</sub>-alkyl,  
R<sup>10</sup> and R<sup>11</sup>, independently of one another, are hydrogen, methyl or ethyl,  
R<sup>12</sup> is selected from methyl and ethyl,  
k is an integer from 0 to 2  
10 and the remaining variables are defined as above.

5. The aqueous dispersion according to any of claims 1 to 4, which comprises at least one oligomer of isobutene, at least one oligomer having an average molecular weight M<sub>n</sub> of from 300 to 5 000 g/mol.  
15

6. A process for the preparation of an aqueous dispersion according to any of claims 1 to 5, wherein (B) and (C) are initially taken, initiator and (A) are added by a feed method, (A), (B) and (C) are subjected to free radical copolymerization 20 with one another, then reacted with (D) and then water is added.

7. The process according to claim 6, wherein reaction with (D) is effected during or after the copolymerization of (A), (B) and, if required, (C) with (D).  
25 8. The use of an aqueous dispersion according to any of claims 1 to 5 for the treatment of fibrous substrates.

9. A process for the treatment of fibrous substrates using an aqueous dispersion according to any of claims 1 to 5.  
30 10. The process according to claim 9, wherein fibrous substrates are selected from leather, textile, paper, board, wood, wood composites, artificial leather, alcantara and lefa.

35 11. The process according to claim 10, wherein the leather is wet-white.  
12. A fibrous substrate treated by a process according to any of claims 9 to 11.  
13. The fibrous substrate according to claim 12, wherein said substrate is leather.  
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14. The leather according to claim 13, wherein said leather is based on wet-white.

15. The use of a fibrous substrate according to any of claims 12 to 14 for the production of articles of clothing or pieces of furniture or automotive parts.

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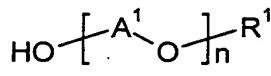
16. A copolymer obtainable by free radical copolymerization of

- (A) at least one ethylenically unsaturated dicarboxylic anhydride, derived from at least one dicarboxylic acid of 4 to 8 carbon atoms,
- 10 (B) at least one oligomer of isobutene, at least one oligomer having an average molecular weight  $M_n$  of from 300 to 5 000 g/mol,
- (C) optionally at least one ethylenically unsaturated comonomer differing from (A),

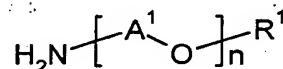
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and reaction with

- (D) at least one compound of the formula I a or I b



I a



I b

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where, in formulae I a and I b,

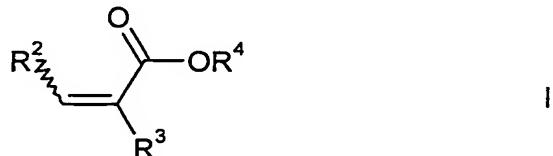
$\text{A}^1$  are identical or different  $\text{C}_2\text{-C}_{20}$ -alkylene,

$\text{R}^1$  is linear or branched  $\text{C}_1\text{-C}_{30}$ -alkyl, phenyl or hydrogen, and

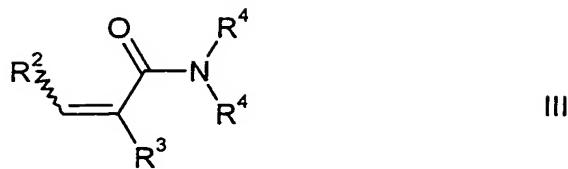
25  $n$  is an integer from 1 to 200,

and optionally hydrolysis.

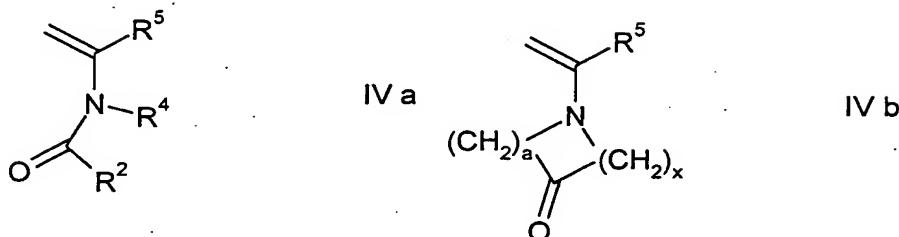
30 17. The copolymer according to claim 16, wherein (C) is selected from ethylenically unsaturated  $\text{C}_3\text{-C}_8$ -carboxylic acid derivatives of the formula II



carboxamides of the formula III



acyclic amides of the formula IV a or cyclic amides of the formula IV b



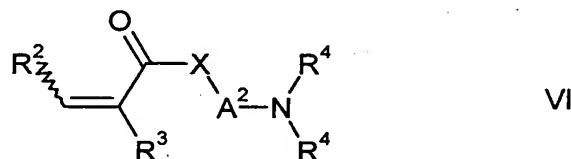
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C<sub>1</sub>-C<sub>20</sub>-alkyl vinyl ethers,  
N-vinyl derivatives of nitrogen-containing aromatic compounds,  
α,β-unsaturated nitriles,  
10 alkoxylated unsaturated ethers of the formula V



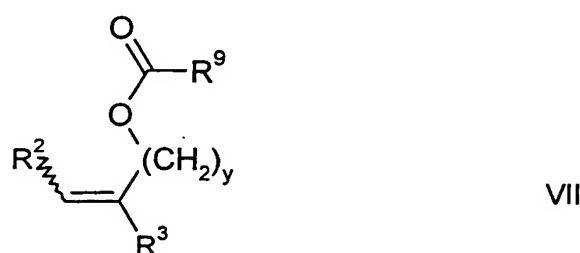
esters or amides of the formula VI

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unsaturated esters of the formula VII

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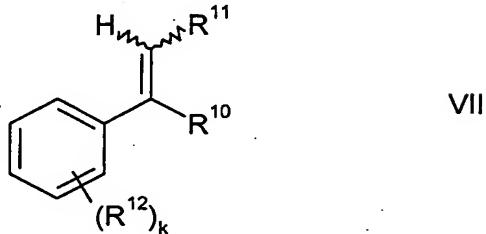


comonomers containing phosphate, phosphonate, sulfate and sulfonate groups,

$\alpha$ -olefins of 3 to 40 carbon atoms,

5

vinylic aromatic compounds of the formula VIII



10 where, in the formulae,

- $A^2$  and  $A^3$  are identical or different and are  $C_2-C_{20}$ -alkylene,
- $R^2$  and  $R^3$  are identical or different and are selected from hydrogen, straight-chain or branched  $C_1-C_5$ -alkyl and  $COOR^4$ ,
- 15  $R^4$  are identical or different and are selected from hydrogen and branched or straight-chain  $C_1-C_{22}$ -alkyl,
- $R^5$  is hydrogen or methyl,
- $x$  is an integer from 2 to 6,
- $y$  is an integer selected from 0 and 1,
- 20  $a$  is an integer from 0 to 6,
- $b$  is an integer from 1 to 200,
- $R^6$  and  $R^7$  are identical or different and are selected from hydrogen and straight-chain or branched  $C_1-C_{10}$ -alkyl,
- $X$  is oxygen or  $N-R^4$
- 25  $R^8$  is  $[A^3-O]_b-R^4$ ,
- $R^9$  are identical or different and are selected from hydrogen and straight-chain or branched  $C_1-C_{10}$ -alkyl,
- $R^{10}$  and  $R^{11}$ , independently of one another, are hydrogen, methyl or ethyl,
- $R^{12}$  is selected from methyl and ethyl,
- 30  $k$  is an integer from 0 to 2

and the remaining variables are defined as above.

- 18. The use of a copolymer according to claim 16 or 17 for the treatment of fibrous substrates.

19. The use of an aqueous dispersion according to any of claims 1 to 5 or a copolymer according to claim 16 or 17 for the impregnation of sheet-like substrates.
- 5
20. A process for the impregnation of sheet-like substrates, wherein a sheet-like substrate is treated with an aqueous dispersion according to any of claims 1 to 5 or with a copolymer according to claim 16 or 17.
- 10    21. The process according to claim 20, wherein the sheet-like substrate is concrete or brick.